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XXVII. *On the state of water and æriform matter in cavities found in certain crystals.* By Sir HUMPHRY DAVY, Bart.
P. R. S.

Read June 13, 1822.

THERE are few enquiries in natural science more calculated to awaken our curiosity, than those relating to the changes which the matter composing the surface of our globe has undergone. The imagination is excited by the magnitude of the operations, by the obscurity of the phenomena, and the remoteness of the time at which they occurred ; and all the intellectual powers are required to be brought into activity to find facts or analogies, or to institute experiments, by which they may be referred to known causes.

The crystallizations constituting the whole of the rocks which are usually called primary, and those found in such abundance, even in the rocks which are termed secondary, prove that a considerable part of the materials of the surface of the globe must have been either fluid or æriform ; for these are the only states from which the regular arrangements of the molecules of bodies constituting crystals, can be produced.

Geologists are generally agreed, that the greater number of the crystalline mineral substances must have been previously in a liquid state ; but different schools have supposed different causes for their solution ; some attributing this effect principally to the agency of water, others to that of heat.

When, however, it is considered, that the solvent power of water depends upon its temperature, and its deposition of solid matters upon its change of state or of temperature ; and that being a gravitating substance, the same quantity must always belong to the globe, it becomes difficult to allow much weight to the arguments of the Wernerians or Neptunists, who have generally neglected, in their speculations, the laws of chemical attraction.

There are many circumstances, on the contrary, favourable to that part of the views of the Huttonians or Plutonists, relating to the cause of crystallization ; such as the form of the earth, that of an oblate spheroid flattened at the poles ; the facility with which heat, being a radiating substance, may be lost and dissipated in free space ; and the observations which seem to show the present existence of a high temperature in the interior of the globe.

I have often, in the course of my chemical researches, looked for facts or experiments, which might throw some light on this interesting subject, but without success, till about three years ago ; when, in considering the state of the fluid and aëriform matters included in certain crystals, it appeared to me, that these curious phenomena might be examined in a manner to afford some important arguments as to the causes of the formation of the crystal.

It is well known that water, and all fluids at usual temperatures, are more expansible by heat than siliceous or other earthy matters ; and supposing these crystals to have been formed, and the water or fluid inclosed in them, at a pressure and temperature not very unlike those of our existing atmosphere, this fluid ought to fill nearly the same space as when

included, and the elastic fluid confined with it, supposing it non-absorbable, ought to be in the same state of density. On the contrary, if the earthy matter and the fluid separated from each other under a much higher temperature than that now belonging to the surface, a certain vacuum might be expected in the cavity from the contraction of the fluid, and if any gas were present, a considerable rarefaction of it; and though, supposing a much higher temperature on the surface of the globe, the atmosphere formed by aqueous vapour must have had much greater absolute weight, which, as liquids are *compressible*, must have influenced the volume of the fluid at the time it was inclosed, a circumstance which would render it impossible to draw any conclusion as to the exact temperature, yet still the experiments appeared to offer, on any view, interesting results; and I was the more desirous of performing them, as I believe the nature of the fluid and aëriform matters included in rock crystals and other siliceous stones, has never been accurately ascertained.

Having purchased some crystals, and having had others committed to my care by the liberality of my Brother Trustees of the British Museum, and of my friend Professor BUCKLAND, I proceeded to make the necessary experiments upon them. It will be improper for me to take up the time of the Society by a minute description of my manipulations. Holes were drilled in the crystals by the use of diamonds, generally by Mr. NEWMAN, under distilled water, or mercury, the gas was expelled by the introduction of wires, and the fluids included in the cavities were drawn out by means of fine capillary tubes, and experiments were afterwards made to determine the space they occupied, which had been accurately measured and

marked upon the crystal. The chemical nature of the fluid and gas was determined by processes which were necessarily difficult from the smallness of the quantities operated upon; but which are too well known to the chemical philosophers of this Society to need description.

The first three crystals that I examined were from Schemnitz, in Hungary; the cavities that they contained were proved not to be permeable to the atmosphere, by exposure to rarefied air, alone, and under water, in the receiver of an air pump, a circumstance which it was necessary always to attend to, in order to render the experiment availing.

A cavity in one of the crystals was pierced under oil, three under distilled water, and one under mercury. In all of them the fluid rushed in when the cavity was opened, and the globule of elastic fluid contracted so as to appear from six to ten times less than before the experiment. The fluid in all the crystals (in two it was minutely examined) was found to be water nearly pure, containing only a minute portion of the alkaline sulphates. The elastic fluid, as well as I could ascertain from the very minute quantities I could procure, appeared to be azote, unmixed with any other substance.

The largest cavity, which was in the crystal put into my hands by Professor BUCKLAND, contained a space equal to 74.5 grains of mercury; the water in it equalled in volume 48.1 grain measures of mercury; and the globule of air, after the experiment, equalled in diameter a globule of mercury weighing 4.2 grains, so that the elastic fluid had contracted at least between six and seven times.

In the other experiments, the cavities being much smaller, the quantities of air and fluid could not be accurately mea-

sured ; but there seemed to be nearly the same relation between the space filled by fluid, and that containing aëriform matter ; and in all of them the contraction of the globule of aëriform matter was evidently greater, and in one instance to less than $\frac{1}{10}$ of its original bulk.

The fourth crystal that I experimented upon was of unknown locality ; but I have reason to believe that it was from Guanaxuato, in Mexico, as it strongly resembled some that Mr. HEULAND showed me from that place. The cavity in it was extremely small, and when pierced into, under distilled water, the globule of gas, from being $\frac{1}{8}$ of an inch in diameter,* diminished so as to be less than $\frac{1}{25}$; so that its rarefaction was much greater in this than in the other instances ; the water was too small in quantity to be minutely examined ; it seemed to be nearly pure, producing a cloudiness barely perceptible in solutions of nitrate of silver and muriate of baryta.

It was an interesting point to ascertain whether the same circumstances occurred in productions found in rocks which have been generally considered as of igneous origin, such as the basaltic rocks in the neighbourhood of Vicenza, the chalcedonies of which so often afford included water. I found it much more easy to make experiments of this kind, and to procure specimens, which were abundantly supplied to me from the same sources as those I have just referred to ; and though some of these specimens proved to be permeable to the atmosphere, and to have been filled with water artificially,

* I have not thought it necessary to refer to the heights of the barometer and thermometer in these experiments, as it is impossible to gain any other than general results, upon quantities in which differences arising from atmospheric temperature and pressure, would be quite unappreciable.

yet many occurred, in which the sides of the cavity were absolutely impervious to air or water.

The results that I obtained were very analogous. Water containing very minute quantities of saline impregnations, occasioning barely a visible cloudiness in solutions of silver and of muriate of baryta, was found to be the fluid; the gas was azote, but it was in a much more rarefied state than in the rock crystals, being between 60 and 70 times as rare as atmospheric air.

The quantity of water was to the void space in greater proportion than in the rock crystals. In the instance in which the most accurate experiment was made, namely, on the great specimen preserved in the collection of the British Museum, and which weighed 380 grains, the quantity of water was 29.9 grains, the space occupied by æriform matter was equal to 11.7 grains of water, the volume of the globule of gas at the common pressure was to that of its rarefied volume as 1 to 63.

It occurred to me that atmospheric air might have been originally the elastic fluid included in these siliceous stones and in the crystals, and that the oxygene might have been separated from the azote by the attraction of the water, and a direct experiment seemed to confirm this idea. A chalcedony which had been bored was placed in water free from air under a receiver, which was exhausted till a portion of gas from the interior of the crystal had escaped into a proper receptacle. This gas examined by nitrous gas, was found to contain nearly as much oxygene as atmospheric air; so that there is every reason to believe that the water had emitted oxygene during the exhaustion.

I endeavoured to find some calcareous secondary rocks, or crystals belonging to them, containing cavities, on which experiments of the same kind might be made; but in a number of trials I have as yet found none impermeable to the atmosphere; and the cavities of such, when bored, are always found to contain atmospheric air in a common state of density.

I was surprised to find that this was the case even with cavities in calcareous spar in the centre of a lime-stone rock; yet these cavities which contained atmospheric air did not fill with water when the stone was placed in water under an exhausted receiver. When however it was dry, and placed in a receiver alternately exhausted and filled with hydrogene, the air that was produced by piercing the cavities, was found mixed with hydrogene; proving that the substance of the stone was permeable to elastic fluid.

I hope soon to be able to make further researches on this subject; but in reasoning upon the vacuum, or rarefied state of the aëriform matter in the cavities of these rock crystals and chalcedonies, it appears difficult to account for the phenomenon, except on the supposition of their being formed at a higher temperature than that now belonging to the surface of the globe; and the most probable supposition seems to be, that the water and the silica were in chemical union, and separated from each other by cooling.

Water in the temperature of the arctic winter is constantly a crystallized body. As a fluid, its solvent powers are increased as its heat becomes higher, and when elastic, the density of its vapour is exalted in proportion to its heat; so that an atmosphere of steam, supplied from an indefinite

source above water, would render it capable of receiving a very high degree of heat. Lime retains water in combination at a heat above 250° FAHRENHEIT ; baryta retains it (even under ordinary pressures) at a strong red heat, and fuses with it. It is extremely likely that a liquid hydrate of silica would exist, under pressure, at high temperatures ; and like all liquid bodies in the atmosphere, would probably contain small quantities of atmospheric air ; and such a supposition only is necessary to account for the phænomena presented by the water in rock crystal and chalcedony.

As, however, steam or aqueous vapour may be considered as having a share in these results, if it be supposed included in the cavity, no exact conclusions can be drawn from the apparent degree of contraction of the water ; particularly as the late ingenious researches of Mr. PERKINS show, that water is much more compressible than was formerly imagined ; and the volume of water, however high its temperature, must be influenced by the pressure to which it is exposed ; so that a certain compressing weight may not only impede, but altogether counteract the expansive force of heat.

Many speculations might be indulged in on this subject, but I shall not at present enter upon them ; and I shall conclude by observing, that a fact, which has been considered by the Neptunists, above all others as hostile to the idea of the igneous origin of crystalline rocks, namely, the existence of water in them, seems to afford a decisive argument in favour of the opinion it has been brought forward to oppose.

June 1, 1822.

APPENDIX.

SINCE the foregoing pages were communicated to the Royal Society, I have made some new experiments on the same subject; all of them, except two, offered results of the same kind as those I have detailed, and upon such I shall not enter: but these two, from their peculiarity, will not, I trust, be thought unworthy of a particular notice.

In examining, with Mr. HEULAND, the beautiful specimens of rock crystals in the collection of CHARLES HAMPDEN TURNER, Esq. I observed one crystal which, Mr. HEULAND informed me, was from La Gardette, in Dauphiné, that contained a considerable cavity, in which there was a viscid brownish liquid, resembling in its appearance and consistence linseed oil. As the void space or cavity filled with aëriform matter appeared considerable in proportion to the fluid, I expressed a desire to pierce the crystal; and Mr. TURNER, hearing of my wish, was so kind as to gratify it in the most polite and liberal manner, by presenting to me the specimen. With Mr. NEWMAN's assistance I made the usual experiments upon it. The cavity was pyramidal, and nearly the third of an inch in diameter. I soon ascertained that the fluid was not water, as it congealed and became opaque at a temperature of 56° . When the crystal was pierced under distilled water, the water rushed in and entirely filled the cavity, so that no other aëriform matter but the vapour of the substance could have been present; the water was rendered white and cloudy, apparently by the substance. I endeavoured to collect some of it for chemical examination, but it was too small in quantity (not equalling in volume $\frac{1}{6}$ of the volume of the cavity,) to be submitted to analysis. It swam on the water, had

no distinct taste, but a smell resembling naphtha; a portion of it taken out mixed with the water, when exposed to heat acted like fixed oil, and it seemed to have a high temperature of ebullition. It inflamed, producing a white smoke.

The fact, of almost a perfect vacuum existing in a cavity containing an expansible but difficultly volatile substance, may be considered as highly favourable to the theory of the igneous origin of crystals: the other experiment is of a nature entirely different, though its result *may* be explained in the same supposition.

In examining a crystal in the collection of the Royal Institution, and which from its characters I believe to be from Capaó d'Olanda, Province of Minas Geraes, Brazil, I observed that the quantity of aëriform matter was unusually small in proportion to the quantity of fluid, in two or three cavities not occupying $\frac{1}{10}$ or $\frac{1}{12}$ of the space; and from the peculiarity of its motion, it appeared to be more likely to be compressed, than rarefied elastic fluid; and in piercing the sides of the cavities I found that this was the case; it enlarged in volume from ten to twelve times; the fluid was water, but the gas was too minute in quantity to be examined.

It will be interesting to ascertain under what circumstances, and in what situations crystals of this kind are found. If they be supposed of igneous origin, they must have been formed under an immense weight of atmosphere or fluid, sufficient to produce a compression much more than adequate to compensate for the expansive effects of heat, a supposition which, in consequence of Mr. PERKINS's experiments, already alluded to, may be easily formed.

July 6, 1822.